

Hydrogenated Microcrystalline Silicon Solar Cells Using Microwave Glow Discharge

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ABSTRACT

Hydrogenated microcrystalline silicon ($\mu\text{c-Si:H}$) materials and solar cells have been obtained using microwave glow discharge at high deposition rates $\sim 20\text{-}30\text{ \AA/s}$. The material properties have been characterized using Raman, X-ray diffraction, small angle X-ray scattering and secondary ion mass spectroscopy. As a reference, $\mu\text{c-Si:H}$ films deposited using radio frequency (RF) and modified very-high-frequency (MVHF) glow discharge were also measured. We find that the microwave deposited $\mu\text{c-Si:H}$ films have lower microcrystal volume fraction and smaller grain size with slight (111) preferential orientation. Microvoid density is higher in the high rate microwave deposited films than the lower rate RF or MVHF deposited films. These characteristics affect solar cell performance and lead to lower short-circuit current density. The best solar cells were made under low microwave power with high H_2 dilution. By optimizing cell structure and deposition condition, we have achieved an initial active-area efficiency of 4.9% in a single-junction $\mu\text{c-Si:H}$ cell.

1. Introduction

$\mu\text{c-Si:H}$ as a low band gap material has attracted significant attention in thin-film silicon solar cell studies due to superior long wavelength response and better stability against light soaking than hydrogenated amorphous silicon (a-Si:H) [1-3]. However, the nature of indirect transition leads to lower absorption coefficient in microcrystalline silicon than in a-Si:H. Therefore, a thick intrinsic $\mu\text{c-Si:H}$ layer is needed to generate high current. From a production point of view, one must have short deposition time to improve throughput, and the need for a thick intrinsic layer demands a high deposition rate for $\mu\text{c-Si:H}$ solar cells to reduce cost. Although conventional RF glow discharge has been successfully used in a-Si:H solar cell production, it is difficult to achieve high rate $\mu\text{c-Si:H}$ deposition. Techniques using RF under high reactor pressure [4] and VHF [1,5] have shown promising results on high rate $\mu\text{c-Si:H}$ deposition, but uniformity for large-area production remains a critical issue. Microwave glow discharge has been successfully used for a-Si:H and a-SiGe:H solar cell deposition at very high rates $\sim 100\text{ \AA/s}$ [6]. We believe that by optimizing plasma conditions in a microwave discharge, there is a good chance to achieve high rate $\mu\text{c-Si:H}$ deposition. In this paper, we report microwave deposited $\mu\text{c-Si:H}$ material properties and solar cell performance, including optimization of plasma parameters and solar cell design.

2. Experimental

A multichamber system with three RF chambers and a microwave chamber is used. Single-junction *nip* solar cells with $\mu\text{c-Si:H}$ as the *i* layer were deposited using microwave on $4\text{ cm}\times 4\text{ cm}$ Ag/ZnO back reflector coated stainless steel substrates. Indium tin oxide (ITO) dots with 0.25 cm^2 active area were deposited on top of the *p* layer as top transparent electrode. Current-voltage characteristics of solar cells were measured under AM1.5 illumination at 25°C . Material structure was characterized using Raman and X-ray diffraction (XRD) spectroscopy, and impurity content using second ion mass spectroscopy (SIMS). Microvoid density was measured by small angle X-ray scattering (SAXS).

3. Results and Discussion

Hydrogen (H_2) dilution is a key technique for $\mu\text{c-Si:H}$ deposition using RF and MVHF glow discharge [1-5]. It has been reported that the required H_2 dilution ratio for $\mu\text{c-Si:H}$ deposition is lower with MVHF than RF glow discharge [7]. Since microwave has a much higher frequency than RF and MVHF, we would expect an even lower H_2 dilution for $\mu\text{c-Si:H}$ deposition using microwave glow discharge. Figure 1 shows open-circuit voltage (V_{oc}) as a function of H_2 and Ar flow rates for microwave deposited solar cells with a fixed SiH_4 flow rate. The high V_{oc} for Ar diluted solar cells indicates amorphous characteristics, and the low V_{oc} for H_2 diluted cells indicates a microcrystalline signature. The transition from amorphous-to-microcrystalline phase occurs at nearly no dilution. This result shows that one can deposit $\mu\text{c-Si:H}$ at very low or even no H_2 dilution. Since H_2 dilution usually reduces deposition rate, the low or no H_2 dilution used for

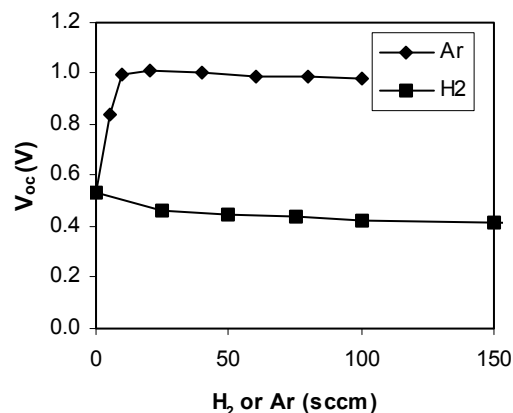


Figure 1. V_{oc} as a function of H_2 and Ar flow rates.

microwave deposition of $\mu\text{c-Si:H}$ has beneficial effect on deposition rate. The reason for low H_2 dilution required is probably due to high atomic H density in the plasma produced by microwave excitation. The transition from amorphous-to-microcrystalline phase depends not only on H_2 dilution, but also on other parameters such as temperature, pressure, and power. We found that high microwave power, high substrate temperature, and low pressure promote microcrystalline formation. However, high quality materials are obtained with relatively low power with certain H_2 dilution.

While a good material property is a necessary condition for achieving high efficiency, a good device design is also critical for solar cell performance. It was reported that there exists an incubation layer before the microcrystalline silicon formation [8]. A seed layer deposited at very high H_2 dilution can reduce or eliminate the incubation layer. Because of the high deposition rate, thickness control of the incubation layer becomes a critical issue for microwave deposited $\mu\text{c-Si:H}$ solar cells. Figure 2 compares of two solar cells deposited with the same recipe for the intrinsic layer, but using (a) an a-Si:H n layer and (b) a $\mu\text{c-Si:H}$ n layer in a ss/Ag/ZnO/nip/ITO configuration. The cell with a $\mu\text{c-Si:H}$ n layer has a significantly improved fill factor (FF) and has no crossover between the dark and light J-V curves. Since a $\mu\text{c-Si:H}$ n layer serves as a seed layer for microcrystalline formation, there is no amorphous incubation layer to affect carrier transport. Similarly, we found that a RF deposited $\mu\text{c-Si:H}$ seed layer also improved cell performance even when an a-Si:H n layer is used.

As shown in Fig. 2, the short circuit current density (J_{sc}) is lower than those obtained from RF and MVHF deposited $\mu\text{c-Si:H}$ solar cells, where $J_{\text{sc}} > 25 \text{ mA/cm}^2$ has been achieved [5]. In order to understand what limits the J_{sc} in microwave deposited $\mu\text{c-Si:H}$ solar cells, we prepared a series of solar cells with different intrinsic layer thicknesses under the same deposition condition. Figure 3 plots the J-V characteristic parameters as a function of intrinsic layer deposition time. J_{sc} increases when the deposition time is in the range of 120 to 300 s, but V_{oc} decreases with increase of deposition time, indicating an evolution of microcrystalline growth. Increasing deposition time further did not lead to further increase of J_{sc} . One puzzling phenomenon is that the FF did not decrease with the increase of intrinsic layer thickness. One explanation could be that the FF is affected by the incubation layer, as indicated by a large V_{oc} in the thinner cell, even through a $\mu\text{c-Si:H}$ n layer was used. The collection in the intrinsic layer may not be a limiting factor for FF. Since the FF does not decrease significantly with the increase of intrinsic layer thickness, we believe that the low J_{sc} was not associated with less efficient collection. Although the real cause of low J_{sc} is not clear at this moment, one possibility is low absorption of long wavelength photons due to low crystal volume fraction and small grain size. By optimizing the deposition conditions, we have been able to deposit $\mu\text{c-Si:H}$ solar cells with improved J_{sc} as shown in Fig. 4. The FF and V_{oc} are poorer due to poor collection, as evidenced by the large difference

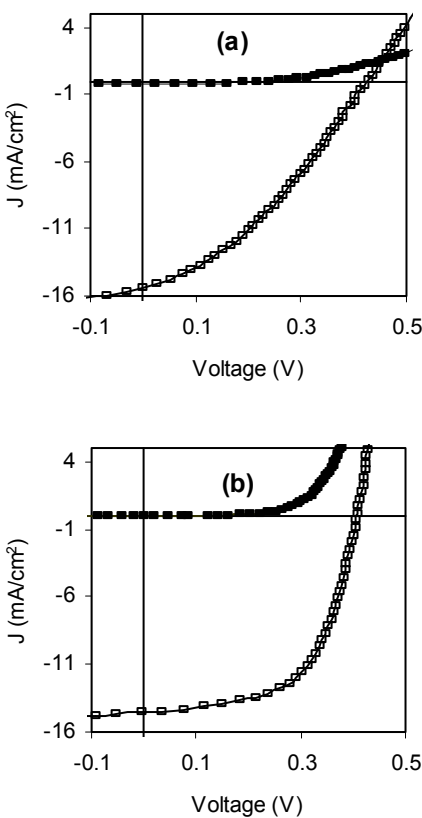


Figure 2. J-V characteristics of microwave deposited $\mu\text{c-Si:H}$ solar cells with (a) an a-Si:H n layer and (b) a $\mu\text{c-Si:H}$ n layer.

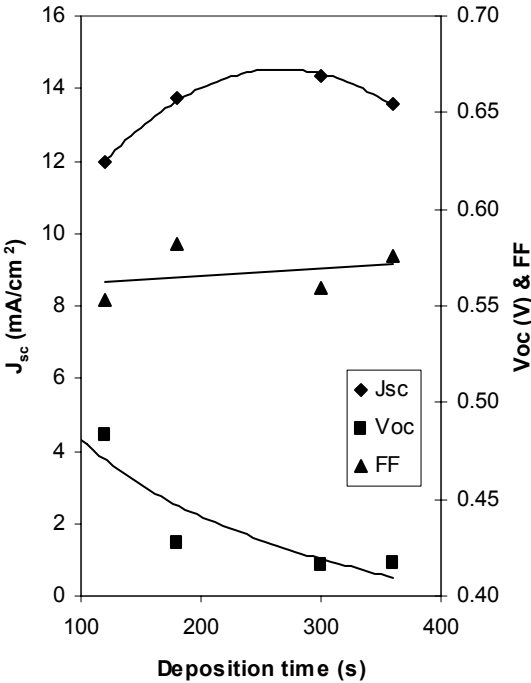


Figure 3. J-V characteristic parameters versus intrinsic layer deposition time.

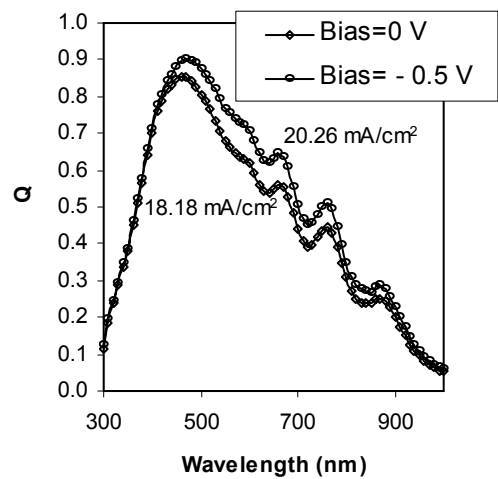


Figure 4. Quantum efficiency of a microwave deposited $\mu\text{c-Si:H}$ solar cell measured under short circuit condition and -0.5 V bias.

between the quantum efficiencies measured at short circuit condition and under a reverse bias. Figure 5 shows the (a) J-V characteristics and (b) quantum efficiency of the best $\mu\text{c-Si:H}$ solar cell deposited using microwave glow discharge. The intrinsic layer was deposited for 210 seconds. An initial active-area efficiency of 4.9% has been achieved.

In order to understand the difference between high rate microwave deposited $\mu\text{c-Si:H}$ and RF or MVHF deposited $\mu\text{c-Si:H}$ films, several characterizations have been made. SIMS analysis showed that oxygen content is around $3\text{--}5\times 10^{18}\text{ atoms/cm}^3$, a level comparable to the lowest reported in the literature [9], even though no gas purifier was used in this study. Therefore, impurity is probably not a main factor limiting the cell performance. XRD and Raman measurements showed lower microcrystal volume fraction and smaller grain size for microwave deposited films. Figure 6 shows XRD spectra for three samples deposited using (A) RF at low rate, (B) MVHF at medium rate, and (C) microwave at very high rate. The strong peaks at 38° and $44\text{--}45^\circ$ are due to the Al foil substrate and the stainless-steel sample holder. The relatively low intensity of the microcrystal peaks, especially the (220) peak, from the microwave deposited film indicates a low microcrystal volume fraction. Table I lists the relative peak intensities (normalized to the (111) peak) and grain size estimated from the width of the peaks by Scherrer equation. The $I_s/I(111)$ is the relative intensity of the shoulder at 27° . Compared to

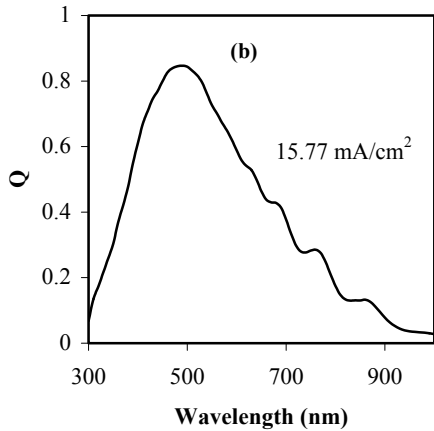
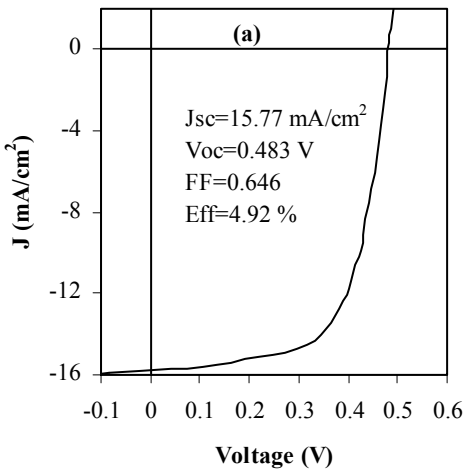


Figure 5. (a) J-V characteristics and (b) quantum efficiency of the best high rate $\mu\text{c-Si:H}$ solar cell made using microwave glow discharge.

the RF low rate and the MVHF medium rate samples, the microwave high rate $\mu\text{c-Si:H}$ has preferential orientation along (111), while the RF low rate sample along (220). The MVHF medium rate sample appears to be close to a random distribution. The grain sizes (parallel to the growth direction) estimated from different peaks on the XRD spectrum are similar for the microwave deposited sample, but significantly enhanced in the (220) and (311) directions in the RF and MVHF deposited samples. The low J_{sc} in the microwave deposited $\mu\text{c-Si:H}$ solar cells could be due to the smaller grain size and lower microcrystal volume fraction. Significant differences in preferential orientation have also

Table I. Relative peak densities and grain sizes estimated from XRD spectra of the RF, MMVHF and microwave deposited $\mu\text{c-Si:H}$ films. A random orientation gives $I(220)/I(111)=0.6$ and $I(311)/I(111)=0.35$.

Sample	I_{220}/I_{111}	I_{311}/I_{111}	I_s/I_{111}	L(111) (nm)	L(220) (nm)	L(311) (nm)
A	1.64	0.21	0.35	8.6	25.3	13.2
B	0.83	0.41	0.10	8.1	10.4	7.7
C	0.28	0.21	0.12	6.0	6.1	5.4

been observed for samples deposited using different techniques, but the effect on solar cell performance is not clear at this moment.

SAXS measurements showed that the high rate microwave deposited $\mu\text{-Si:H}$ film (C) have high microvoid density than other low rate samples (A,B). The sample C has 3.1% microvoid density, while sample A only 0.7%. The high microvoid density may result in high defect density and poor cell performance.

4. Summary

Microwave glow discharge has been used to deposit $\mu\text{-Si:H}$ solar cells at very high rates $\sim 20\text{-}30 \text{ \AA/s}$. An initial active-area efficiency of 4.9% has been achieved. Compared to RF and MVHF deposited $\mu\text{-Si:H}$ solar cells, the most significant drawback is lower J_{sc} . Although the reason for low J_{sc} has not been fully understood at this moment, Raman and XRD showed a lower microcrystal volume fraction and smaller grain size than those deposited using RF and MVHF. In addition, SAXS analysis showed a 3% microvoid density in microwave deposited $\mu\text{-Si:H}$ films, larger than RF and MVHF deposited $\mu\text{-Si:H}$ films. Further optimizations of plasma condition and cell design are under way.

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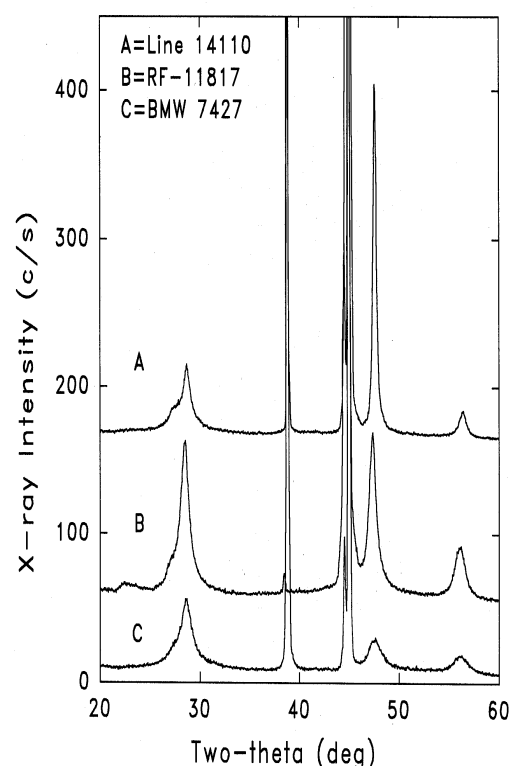


Figure 6. XRD spectra of $\mu\text{-Si:H}$ films deposited using (A) RF at a low rate, (B) MVHF at a medium rate, and (C) microwave at a high rate.

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